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419387

6 Sept 63

RSIC-52

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OF LIQUIDS AND THE ACCOMMODATION COEFFICIENTS

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From

Zhurnal Fizicheskoi Khimii, USSR,
13, No. 11, 1635-1641 (1939)

Redstone Scientific Information Center

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Translated from the Russian by
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Redstone Arsenal, Alabama

THE RELATIONSHIP BETWEEN THE SURFACE ENERGY OF LIQUIDS AND THE ACCOMMODATION COEFFICIENTS

by

M. Baranaev

During equilibrium of a liquid phase with vapor, the number of molecules breaking off from the surface of a liquid and changing into vapor due to thermal motion is equal to the number of molecules which, at the same time, change back from vapor into liquid condensing on its surface.

The number of molecules condensing on the surface of a liquid at 1 cm² per sec. (N_k) may be easily found by means of Knudsen's known formula.

$$N_k = N \alpha p_0 (2\pi MRT)^{-\frac{1}{2}}. \quad (1)$$

Here, α is the accommodation coefficient¹⁾, i. e., a coefficient indicating which part of the molecules striking upon the surface of a liquid phase condenses on this surface; N is Avogadro's number; p_0 is the pressure of the saturated vapor; M is the mass of a gram-molecule; R is the gaseous constant; T is the absolute temperature.

All values entered on the right side of formula (1), except α , are easily determined by experiments. Consequently, by knowing α , the number of molecules breaking off from the surface of a condensed phase may be easily found by calculating an equal number of condensing molecules from formula (1).

¹⁾ This term is presented by Knudsen [1].

The number of molecules breaking off from the surface of a condensed phase during an equilibrium of the latter with its own vapor, generally speaking, is not equal to the number of molecules, breaking off from the surface at the time of the evaporation of a given substance in a vacuum. Thus, during evaporation of solid bodies in a vacuum, the "outer" atoms (molecules) of a crystal lattice vibrating around the centers of equilibrium located at the lattice points break off one after another. But during equilibrium of a solid crystal with vapor, not all molecules located on the surface occupy their "rightful" place. Some are in an adsorbed like state and migrate along the surface until they again re-enter the gaseous phase or positively attach themselves to the lattice points /1, 2, 3/. In this manner these molecules are also active in the process of exchange between the gaseous and condensed phases, i. e., they break off and then again settle on the surface of the crystal. Conditions of the break off of such "incompletely condensed" (adsorbed) molecules may not coincide with the conditions of break off of the molecules from the lattice itself.

However, in the case of liquids which do not have a stable crystal lattice, the molecules "which have not yet taken their place in the lattice" cannot be distinguished from the molecules forming the lattice itself, because all molecules of the liquid very frequently change their centers of vibration, migrating in this manner from one lattice point to the other. The time intervals between two such transitions of each molecule have the same order of magnitude as the period of vibrations /4/.

Thus, it may be considered that all molecules appearing on the surface of the liquids in any way are completely equivalent, and this means that the quantity of molecules breaking off from the surface during the absence of vapor over it, i. e., in a vacuum, is equal to the quantity of molecules breaking off from the surface which is in contact with saturated vapor /5/. The vapor molecules in themselves evidently cannot significantly change the conditions of the break off from the surface of the molecules of the liquid. The influence of the vapor molecules on each other, and consequently on the molecules on the surface of the liquid, is negligible in comparison with the action of the liquid molecules themselves. This may be easily seen by comparing the heat of liquid evaporation with the heat of vapor expansion in a vacuum. Thus, the evaporation rate for liquids in a vacuum is equal to the rate of condensation as calculated by Knudsen's formula (1). For certain practical calculations it is often necessary to know the rate of evaporation in a vacuum. In order to be able to calculate this rate in accordance with Knudsen's formula, it is necessary, as already indicated, to know the coefficient α . However, up to now the only method of determining coefficient α was by having it calculated through the known evaporation rate in a vacuum.

Langmuir /3/ considers that coefficient α should always equal 1, however, there are reasons for considering that this is not completely right. Alty /6/ found that coefficient α equals approximately 0.04 for water, while for carbon tetrachloride α equals 1. Alty also indicated that here a role is placed by the symmetric structure of molecules

CCl_4 . This viewpoint is substantiated by the fact that the mercury molecules, the accommodation coefficients of which are almost equal to 1, are also symmetric.

It is known that asymmetric molecules are mainly oriented on the surface of the liquid, which causes somewhat of a decrease in the surface energy in comparison with a newly developed surface. Many investigators /7/ determined that surface tension on a newly developed surface of water was considerably higher than that on an "old" surface. Thus, with each hit on the liquid surface by a nonoriented molecule from the vapor phase the surface energy should somewhat increase. If we assume that only those vapor molecules which possess energy E sufficient to cause this increase, would strike the surface layer, then by using e — Boltzmann's law, it is possible to calculate the number of molecules N_k , condensing per second on 1 cm^2 of the surface.

$$N_k = \int_{U_0}^{\infty} \frac{N p_0}{RT \sqrt{\frac{2\pi RT}{M}}} \cdot U \cdot e^{-\frac{MU^2}{RT}} dU. \quad (2)$$

Here U_0 is the velocity of the molecules corresponding to energy E , i. e., $E = \frac{MU_0^2}{2}$; from here and formula (1) and (2) we get:

$$\alpha = e^{-\frac{E}{kT}} \quad (3)$$

Thus, condensation of only

$$N_k = N p_0 e^{-\frac{E}{kT}} (2\pi MRT)^{-\frac{1}{2}} \text{ molecules/cm}^2 \cdot \text{sec.} \quad (4)$$

The remainder will break away from the liquid surface /8/.

The result of molecular orientation in the surface layer is also

due to the deviation from "Stefan's law" /9/, according to which the surface energy of liquid must be equal to half of the heat of evaporation. Stefan presented this law, assigning a spherical symmetry to the liquid molecules. Actually, as shown by the calculations /10/, considerable deviations from "Stefan's law" are observed, and these are greater as the liquid molecules are less symmetrical (Table 1).

T a b l e 1

Substance	Internal evaporation temperature, at $\theta^1)=0,7 T_{cr}$	Surface E_s energy	$\frac{E_s}{\lambda_i}$
	In ergs per molecule		
CCl_4	$40,2 \cdot 10^{-14}$	$18,2 \cdot 10^{-14}$	0,452
C_6H_6	$41,7 \cdot 10^{-14}$	$18,4 \cdot 10^{-14}$	0,441
C_6H_5Cl . . .	$48,8 \cdot 10^{-14}$	$20,3 \cdot 10^{-14}$	0,417
C_2H_5OH . . .	$59,3 \cdot 10^{-14}$	$11,2 \cdot 10^{-14}$	0,186

The value of the deviations from "Stefan's law" is evidently determined by a decrease of the surface energy during the orientation of the molecules /11/. Thus, by calculating the difference (Δ) between the fraction of the heat of evaporation²⁾ corresponding to the surface energy $\left(\frac{E_s}{\lambda_i}\right)$ for liquids with symmetric molecules, and with the same value for liquids with asymmetric molecules the decrease in the value of surface energy E occurring during the orientation of molecules of the surface layer may be estimated approximately.

We performed such calculations. We selected CCl_4 as the liquid

1) θ - Corresponding temperature

2) The internally concealed evaporation temperature λ_i is considered here.

with symmetric molecules. We compared it with methyl, ethyl and propyl alcohols, benzene, toluene and chloroform. For calculations, the heat of evaporations and surface energies of liquids were taken at the temperatures when both liquids were in corresponding states. The critical temperatures of all liquids used by us, lay fairly close to each other - in an interval of 134° (excluding water - in an interval of 80°). The number of molecules n_s coming into 1 cm² of the surface layer was determined by the method which Harkins and Roberts' /14/ used in their work; i. e., it was assumed that

$$n_s = \left(\frac{dN}{M} \right)^{\frac{2}{3}} \quad \text{molecules/cm}^2, \quad (5)$$

where d is the density of g/cm³, M is the mass of a gram-molecule in g, and N is the Avogadro number.

The area occupied by a molecule of methyl alcohol on the surface considered /12/ to equal 21 Å²).

The results of calculations are given in columns 1 - 5 of Table 2¹⁾.

By substituting the obtained value of E into formula (3) it is possible to estimate the order of magnitude α . The results are given in the 6th column of Table 2.

It is interesting to compare the values calculated in this manner with the experimental data. As seen from Table 2, α equals

1) Heats of evaporation, critical temperatures, densities and surface tensions were taken from the Int. Crit. Table (1933) for calculations.

2) According to Harkin's and Robert's data.

Table 2

Substance	Temp- of liq- uid T in °K	Corres- ponding Temp. θ	$\Delta = \frac{E_{CCl_4}}{\lambda_1} - \frac{E_1}{\lambda_1}$	$E = \lambda_1 \Delta$ in erg/ molecules · 10 ¹⁴	$\alpha = e^{-\frac{E}{kT}}$
1	2	3	4	5	6
H ₂ O ¹⁾	323	0,500	0,200	13,92	0,033
H ₂ O	283	0,437	0,189	12,95	0,034
CH ₃ OH	271	0,527	0,197	11,66	0,04
C ₂ H ₅ OH	273	0,527	0,227	15,05	0,02
C ₃ H ₇ OH	283	0,527	0,217	15,40	0,02
C ₆ H ₆	283	0,504	0,014	0,738	0,77
C ₆ H ₅ CH ₃	283	0,477	0,038	1,40	0,6
CHCl ₃	273	0,510	0,053	1,72	0,2

0.034 for water, and Alty's /6/ data for water is $\alpha = 0.036$. Such concurrence is even somewhat unexpected.

We performed a series of tests on the determination of α for methyl, ethyl and propyl alcohol, also for benzene, toluene and chloroform. All substances (analytically pure) were dried and distilled twice.

Tests were performed with fractions distilled at the following temperature intervals.

In addition, benzene was frozen twice. Freezing temperature was 5.85° C.

The method of our tests was partially adopted from Alty /13/. The method of direct measurement of the evaporation rate in a vacuum, used by Kundsén, was regrettably not suitable for the determination of coefficient α in such comparatively high volatile liquids as water and carbon tetrachloride. If an attempt were made to evaporate water in the vacuum so that it's surface temperature would be 20° C, the

Suostance	$t, ^\circ\text{C}$	P_{mm} Bar/ Press.
$\text{CH}_3\text{OH} \dots$	64,5—65,7	764
$\text{C}_2\text{H}_5\text{OH} \dots$	78,0—78,2	752
$\text{C}_2\text{O}_2\text{OH} \dots$	96,5—97,0	745
$\text{C}_2\text{H}_6 \dots$	80,0—80,1	757
$\text{C}_2\text{H}_5\text{CH}_3 \dots$	110,0—110,1	746
$\text{CHCl}_3 \dots$	59,8—60,8	743

overheating of the liquid phase would become so considerable that it would be impossible to prevent boiling. The evaporation process alone would, in such an instance, occur so rapidly that it would make it difficult to perform measurements.

Therefore, we determined the rate of evaporation in a vacuum by an indirect way. The liquid was evaporated in the atmosphere of its vapor under pressure p , being less than the pressure of saturated vapor p_0 , corresponding to the temperature of the liquid surface, which was measured by means of a thermocouple.

In this instance the evaporation rate W equaled the difference between the evaporation rate in a vacuum and the rate of return condensation, i. e.

$$W = \alpha p_0 \sqrt{\frac{M}{2\pi RT}} - \alpha p \sqrt{\frac{M}{2\pi RT}}. \quad (6)$$

From here

$$\alpha = \frac{W}{(p_0 - p) \sqrt{\frac{M}{2\pi RT}}}. \quad (7)$$

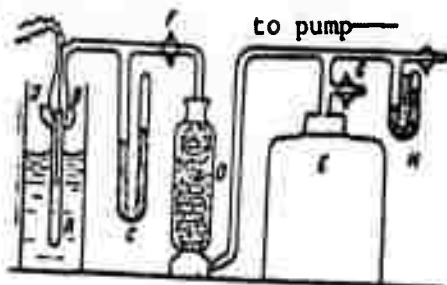


Fig. 1

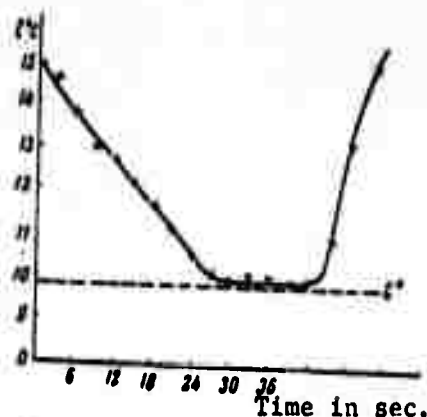


Fig. 2. The initial interval 1.15 mm of the thermocouple junction from the meniscus surface. Subsiding rate of the meniscus 0.0386 mm/sec.

A schematic drawing of the device which we used is shown in Fig. 1.

The liquid under investigation was poured into tube A and placed in a water-thermostat. By means of a flooded mercury section B, tube A was connected to an outlet tube and manometer C. Temperature of the liquid was measured by means of a copper-constantan thermocouple. The little wires at the thermocouple junction were 0.2 mm in diameter. The pressure, under which the evaporation occurred, was measured by manometer C. The height of the mercury level was determined by means of a microscope with an accuracy up to 0.02 mm. Air was evacuated from the device by means of an oil pump. Constant pressure in the device was maintained by means of cocks F and G, buffer E, and regulating manometer H. Column D, filled with activated carbon, absorbed the vapor of the investigated substance. The evaporation rate was determined by subsiding of the liquid level in tube A. Level conditions were determined by means of a microscope with an accuracy of up to

0.03 mm. Each measurement of the evaporation rate was repeated 3 - 4 times. Average data is given in Table 3. The results of the repeated tests differ from each other by 3 - 4%. The value of the evaporating surface was determined as described¹⁾ in our previous article /14/. Thin wires of the thermocouple insignificantly distorted the meniscus surface, hardly changing its value. In order to be sure of this, in practically all our tests we determined the rate of evaporation very shortly prior to and immediately after disconnection of the thermocouple end from the subsiding surface of the meniscus. Within the limits of an error in the test, the result obtained was identical.

The temperature of the evaporating surface was determined by a method, analogous to the one described by Alty's /15/. During evaporation of the liquid when the meniscus gradually subsided, the thermocouple junction, which had been in contact with and was finally disconnected from the meniscus and readings of the galvanometer, connected to the thermocouple were observed. One of the curves expressing the temperature on the end of a thermocouple is shown in Fig. 2. Temperature t_0 corresponding to the contact of the thermocouple junction with the surface was used for calculating the temperature of the liquid surface. Somewhat of a stoppage of temperature near t_0 is explained by the fact that, during disconnection of the thermocouple from the liquid, the surface slightly deformed and appeared as if it pulled away with the wires.

¹⁾ The meniscus surface was considered as equal to the curve of the surface of a spherical segment having with the meniscus a joint line of contact with the walls of the tube and a joint point inside the meniscus.

The test results are shown in Table 3.

Table 3

Substance	Surface Temp. t_0 in $^{\circ}\text{C}$	Press. of saturated vapor ¹⁾ corresponding to t_0 p_t in mm Hg	Pressure in device p in mm Hg	Evaporation rate W in $\text{g}/\text{cm}^2/\text{sec.}$	$\alpha_{exp} = \frac{W}{(p_t - p)} \sqrt{\frac{M}{2\pi RT}}$	$\alpha_{cal} = e^{-\frac{E}{RT}}$
Methyl alcohol	3,5	21,0	18,5	$2,15 \cdot 10^{-3}$	0,045	0,04
	2,5	22,5	20,0	$2,15 \cdot 10^{-3}$	0,045	
Ethyl alcohol	2,0	10,6	7,1	$1,75 \cdot 10^{-3}$	0,020	
	0,0	12,2	8,9	$1,50 \cdot 10^{-3}$	0,020	0,02
Propyl alcohol	4,7	5,15 ²⁾	4,12	$1,02 \cdot 10^{-3}$	0,037	
Benzene	6,6	42,0	41,90	$2,65 \cdot 10^{-3}$	0,86 ³⁾	0,7
	6,3	41,5	41,60	$2,85 \cdot 10^{-3}$	0,93	
Toluene	5,5	9,86	9,73	$3,6 \cdot 10^{-3}$	0,83 ³⁾	0,6
	9,1	12,22	12,08	$1,8 \cdot 10^{-3}$	0,45	
Chloroform	2,0	67,3	66,77	$3,9 \cdot 10^{-3}$	0,16	0,2

The comparatively small discrepancy between the values of accommodation coefficients, calculated by us (α_{cal}) and obtained experimentally (α_{exp}) indicate that for determination of the order of magnitude α , the method, indicated above by us, may be applied.

Summary

1. Attempts were made to find the relationship between the coefficient of accommodation and the surface energy of liquid.

1) Values found by data from the tables (Int. Crit. Tabl., 3, 216, 1933) by means of interpolation.

2) By Mundel's data /16/.

3) Large discrepancies between values α_{cal} obtained for benzene and toluene can be explained by the very small difference of $(p_t - p)$ in this case, and also the fact that errors in measurements strongly distort the results.

2. On the basis of the obtained relationship between the coefficient of accommodation and the rates of evaporation in a vacuum for methyl, ethyl and propyl alcohols, benzene, toluene and chloroform, were calculated.

3. Experimental verification of the calculation results was performed by means of measuring the evaporation rates of the above indicated liquids in a vacuum.

4. The values of accommodation coefficients obtained experimentally satisfactorily coincided with calculated values.

The values of accommodation coefficients obtained by Alty /5, 13/ also coincided with values α , calculated by us.

Submitted to Editor
13 June 1939.

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